Structures of Sesquiterpenes of *Curcuma aromatica* SALISB. II.[1] Studies on Minor Sesquiterpenes

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Further study on the sesquiterpenes from *Curcuma aromatica* (Zingiberaceae) has resulted in the isolation of eleven minor sesquiterpenes, 1—11 having guaiane, seco-guaiane and germacrane skeletons, and their structures were elucidated by proton nuclear magnetic resonance (^{1}H-NMR) and ^{13}C-nuclear magnetic resonance (^{13}C-NMR) spectroscopy, as well as chemical investigation. The stereochemistry of these sesquiterpenes was elucidated by 2D NMR techniques such as ^{1}H–^{1}H correlation (COSY) and nuclear Overhauser effect correlation (NOESY), and circular dichroism (CD) spectroscopy.

Keywords *Curcuma aromatica*; Zingiberaceae; sesquiterpene; germacrane-type compound; guaiane-type compound; seco-guaiane-type compound; ^{13}C-NMR spectrum; circular dichroism

In the course of our studies on the isolation and the structural elucidation of sesquiterpenes from *Curcuma* spp., we previously reported the structures of ten sesquiterpenes[1] isolated from *C. aromatica*. A further study on the sesquiterpenes of the rhizomes of the plant by mean of repeated precise silica gel (SiO_2) column chromatography and high-performance liquid chromatography (HPLC) has resulted in the isolation of eleven minor sesquiterpenes, named epiprocurcumenol (**1**), isoprocurcumenol (**2**), neoprocurcumenol (**3**), (4*S*)-13-acetoxydehydocurdione (**4**), (4*S*)-13-hydroxydehydrocurdione (**5**), (4*S*,5*S*)-13-hydroxygermacrone 4,5-epoxide (**6**), (4*S*,5*S*)-13-acetoxygermacrone 4,5-epoxide (**7**), (4*S*,5*S*)-12-acetoxygermacrone 4,5-epoxide (**8**), acetoxyneocurdione (**9**), curcumadione (**10**) and isocurcumadione (**11**) along with the previously known 13-hydroxygermacrone (**12**),[2] isolated from *C. zedoaria*. Their structures were elucidated by means of spectroscopical methods, especially carbon thirteen nuclear magnetic resonance (^{13}C-NMR) and 2D NMR spectroscopy, and chemical investigations.

Epiprocurcumenol (**1**) gave the molecular formula, $C_{15}H_{22}O_2$, from the mass spectrum (MS). The proton nuclear magnetic resonance (^{1}H-NMR) and ^{13}C-NMR spectra of **1** showed the presence of four methyl groups, one of which was considered to be a tertiary methyl group (δ 1.37 (s)), an olefinic proton (δ 5.91 (br s)) having a long-range coupling with a vinyl methyl group, three vinyl methyl groups (δ 1.84, 1.94 × 2) and the cross-conjugated dienone group (δ 196.1) like that found in procurcumenol (**13**),[3] whose stereostructure was determined by Kitagawa *et al.*[4] These data indicated that **1** should be a stereoisomer of **13**. From the transannular cyclization[5] mechanism of transformation of the key intermediate, (4*S*,5*S*)-germacrone 4,5-epoxide[6] (**14**), **1** should be the epimer of **13** at C-1 (shown in Chart 2). In the ^{13}C-NMR spectrum of **1**, the signals of C-1, C-7 and C-8 were shifted to upper field by a few ppm

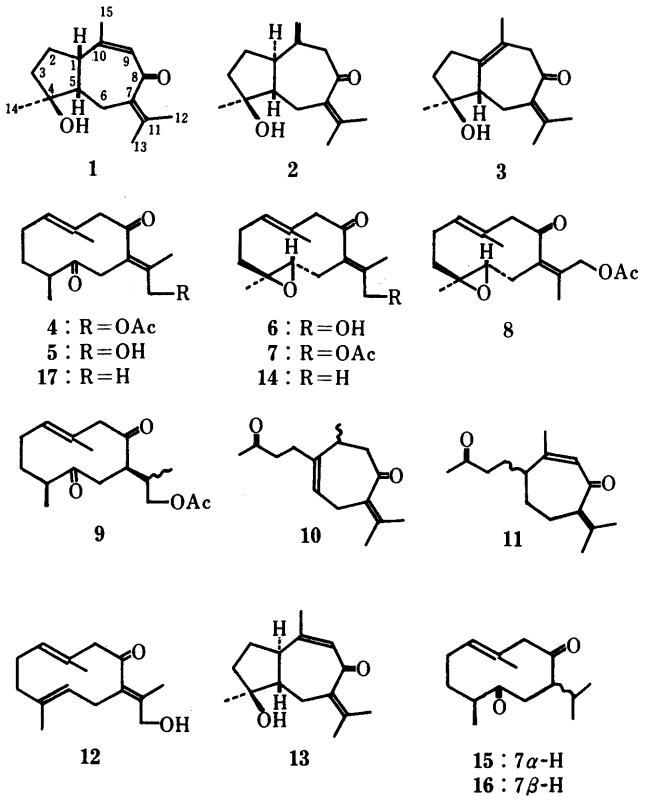

Chart 1

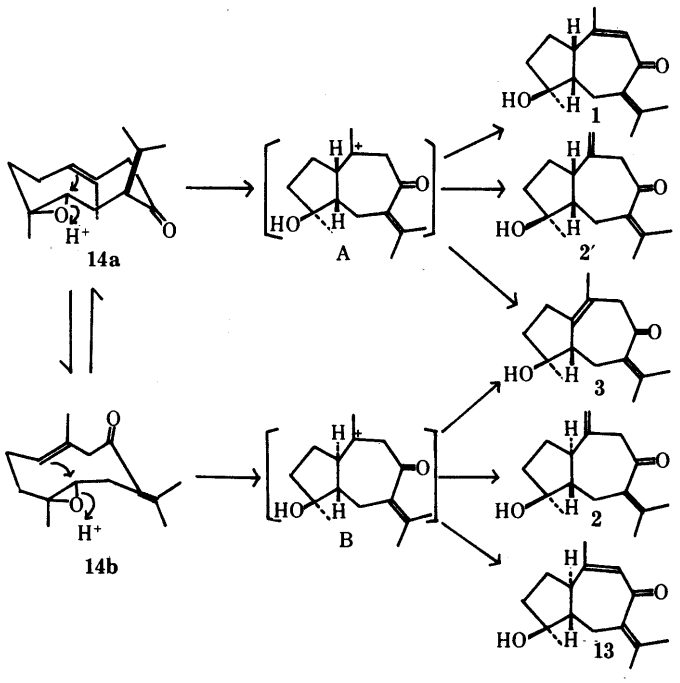

Chart 2

(4.1, 2.1, 3.8), and that of C-15 was shifted downfield by a few ppm (2.0), compared with those of **13**. The other carbon spectral data for **1** appeared at similar chemical shifts (shown in Table I). From these data, the structure of epiprocurcumenol was supposed to be **1**, including the absolute configuration.

Isoprocurcumenol (**2**), mp 99.5—100.5 °C, and neoprocurcumenol (**3**), mp 77—79 °C, showed the same molecular formula, $C_{15}H_{22}O_2$, in the MS. From the ^{1}H- and ^{13}C-NMR spectra, the structures of isocurcumenol and neocurcumenol were supposed to be **2** and **3**. The absolute configuration of **3** was confirmed by transformation from **14**. The absolute configuration of isocurcumenol was also considered to be **2** or its C-1 epimer from the transannular cyclization mechanism[5] as shown in Chart 2. Kitagawa *et al.*[4] reported the transformation of **14** into procurcumenol, GU-2[7] and GU-3[7] by treatment with acid, and their structural elucidation included the stereochemistry. They found GU-2 in *C. zedoaria*. The spectral data of **2** and **3** were identical with the reported data of GU-2 and GU-3. We also obtained **2** and **3** along with the other several products from **14** by treatment with acid[8] and these products (**2** and **3**) were identical with the natural **2** and **3** (including optical rotations).

(4*S*)-13-Acetoxydehydrocurdione (**4**), mp 77—78 °C, gave the molecular formula $C_{17}H_{24}O_4$, which was supported by the ^{13}C-NMR spectrum. The infrared (IR) spectrum of **4** showed the presence of an ester group (1740 cm^{-1}) and an ordinary carbonyl group (1715 cm^{-1}). The ^{13}C-NMR spectrum of **4** showed the presence of two carbonyl groups (δ 210.3, 206.0), an acetoxyl group (δ 20.8, 170.6) and an acyloxymethyl group (δ 64.5). The presence of the acetoxymethyl group was also suggested by the ^{1}H-NMR spectrum (δ 2.05 (3H, s), 4.47 (1H, d, J=12.9 Hz), 4.76 (1H, d, J=12.9 Hz)). The ^{13}C-NMR spectrum of **4** showed almost the same chemical shifts as those of dehydrocurdione (**17**) (Table I). These data suggested that **4** is an acetoxy derivative of **17** at C-12 or C-13. The ^{1}H–^{1}H correlation (COSY) spectrum of **4** confirmed the assignments of proton signals. The position of the acetoxy group of **4** was determined from the nuclear Overhauser effect correlation (NOESY) spectrum. One of the methylene protons of the acetoxymethyl group had cross peaks with the proton of methylene group at C-6. These indicated that the acetoxy group is located at C-13. The circular dichroism (CD) spectrum of **4** showed a positive Cotton effect at 317 nm based on the n→π* transition of a β,γ-unsaturated ketone,[9] as in the case of **17** (Fig. 1), so the absolute configuration of C-4 of **4** was concluded to be *S*, like that of **17**.

(4*S*)-13-Hydroxydehydrocurdione (**5**), colorless oil, gave the molecular formula $C_{15}H_{22}O_3$, from the MS. The ^{1}H-NMR spectrum of **5** showed the presence of a secondary methyl group (δ 1.04 (d, J=6.6 Hz)), two vinyl methyl groups (δ 1.69, 1.84) and an olefin proton (δ 5.12 (t, J=6.5 Hz)). The ^{13}C-NMR spectrum of **5** showed the characteristic signals for dehydrocurdione (**17**) except for the presence of a hydroxymethyl group (δ 63.2) instead of a methyl group. These results indicated that **5** is a hydroxy derivative of **17**. Acetylation of **5** gave an acetate which was identical with **4**.

The CD spectrum of **5** showed a similar positive Cotton effect to that of **4** (Fig. 1), and thus **5** was concluded to be (4*S*)-13-hydroxydehydrocurdione.

(4*S*,5*S*)-13-Hydroxygermacrone 4,5-epoxide (**6**), an oil, gave the molecular formula $C_{15}H_{22}O_3$, from the MS. The ^{13}C-NMR spectrum of **6** showed the presence of a hydroxymethyl group (δ 62.2), an epoxide group (δ 61.0, 64.5) and four olefinic carbons (δ 129.9, 135.1, 126.2, 136.7). From these data **6** was considered to be the 12- or 13-hydroxy derivative of **14**. The ^{1}H-NMR spectrum of **6** also supported this structure. The comparison of the ^{13}C-NMR spectrum of **6** with that of **14** indicated that all carbon chemical shifts of **6** were identical with those of **14** except for those of C-11, C-12 and C-13 (Table I). 13-Hydroxygermacrone (**12**) was epoxidized by *m*-chloroperbenzoic acid to give racemic 13-hydroxygermacrone 4,5-epoxide, which was identical with the natural **6** in terms of thin-layer chromatographic (TLC) and HPLC behavior and ^{1}H-NMR spectrum. These results indicated that **6** is the 13-hydroxy derivative of germacrone 4,5-epoxide (**14**).

(4*S*,5*S*)-13-Acetoxygermacrone 4,5-epoxide (**7**), an oil, gave the molecular formula $C_{17}H_{24}O_4$, from the MS. The ^{13}C- and ^{1}H-NMR spectra of **7** showed the presence of an acetyl group (δ 2.10 (s) and 170.6, 20.6), a tertiary methyl group (δ 1.05 (s) and 15.8) on an epoxide carbon, an epoxide group (δ 60.6, 64.1), a trisubstituted olefin group (δ

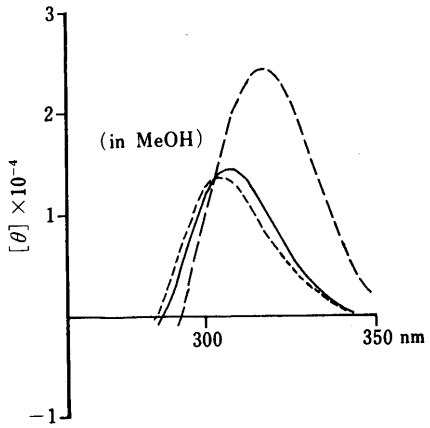

Fig. 1. CD Spectra of Dehydrocurdione Derivatives
4, ----; **5**, ——; **17**, ------.

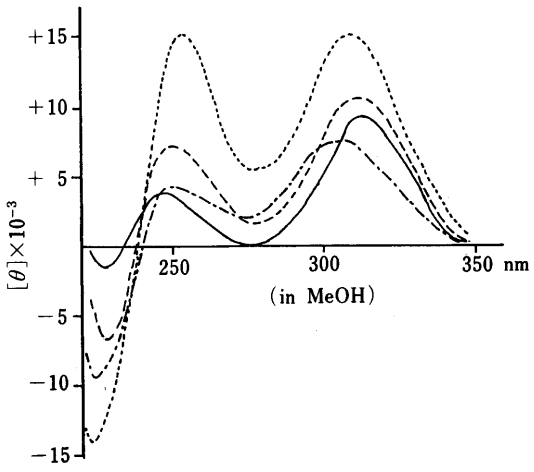

Fig. 2. CD Spectra of (4*S*,5*S*)-Germacrone 4,5-Epoxide Derivatives
7, ——; **6**, ----; **14**, ------; **8**, ---.

TABLE I. ^{13}C-NMR Data for the Sesquiterpenes[a]

	1	2	3	4	5	6	7	8	9	10	11	13	14	15	17
C-1	46.4	51.1	122.2	133.1	133.1	129.9	130.3	130.0	131.1	140.0	41.3	50.5	129.7	131.1	132.7
C-2	26.7[b]	24.7[b]	27.7	26.7	26.7	24.4	24.5	24.6	25.5	27.8	30.0	26.9	24.5	25.5	26.2
C-3	28.4	28.2	28.2	34.2	34.1	37.3	37.7	37.5	33.1	42.6	43.8	28.6	37.7	32.8	34.1
C-4	81.7	79.7	80.0	47.3	47.8	61.0	60.6	60.6	46.2	208.1	208.1	80.2	60.4	45.8	46.4
C-5	54.6	58.7	54.1	210.3	213.4	64.5	64.1	63.9	209.1[b]	121.1	31.2	54.0	64.3	210.2	210.6
C-6	38.3	39.8	39.0	34.2	42.9	28.7	29.4	30.0	40.9	30.2	32.2	39.9	29.7	42.1	43.4
C-7	134.5	134.5	135.2	128.8	129.0	126.2	126.3	126.4	47.8	134.7	126.7	136.6	126.7	52.6	129.8
C-8	196.1	203.2	203.8	206.0	207.0	204.2	203.3	202.9	211.9[b]	205.1	191.0	199.9	204.3	212.5	206.4
C-9	129.0	53.8	51.1	56.7	56.8	54.9	55.1	55.6	54.9	48.6	128.8	129.2	55.4	55.3	56.8
C-10	154.7	141.3	137.2	132.6[b]	131.4	135.1	131.9	132.5	129.4	35.0	162.4	155.1	133.7	129.1	130.0
C-11	140.8	144.0	138.5	133.6[b]	137.6	136.7	138.3	138.0	35.0	143.7	144.8	136.3	133.9	30.9	136.9
C-12	21.6	21.9	21.8[b]	17.2	18.4[b]	18.0	18.4	65.1	14.5	19.1[b]	22.4[b]	21.2	20.3	20.2	20.9
C-13	22.7	22.7	21.8[b]	64.5	63.2	62.2	64.1	16.3	67.4	22.6[b]	22.9[b]	22.4	22.6	21.1	22.0
C-14	24.8	24.3[b]	22.6[b]	18.2	18.3[b]	15.6	15.8	15.9	17.8	22.2	22.2[b]	23.3	15.8	18.2	18.3
C-15	26.3[b]	111.3	21.2[b]	16.2	16.1	16.8	17.6	17.0	17.9	19.1[b]	23.0[b]	24.3	17.0	18.2	16.2
CO				170.6			170.6	171.0	170.6						
CH_3				20.8			20.6	20.7	20.7						

a) Measured in $CDCl_3$. b,c) Assignments may be interchangeable within the same column.

5.23 (t, J=7.5 Hz) and 130.3, 131.9) and a tetrasubstituted olefin group (δ 126.3, 138.3) conjugated with a ketone (δ 203.3). The presence of a conjugated ketone was also supported by the IR spectrum (1680 cm^{-1}). These facts suggested that **7** is the acetoxy derivative of **14**. 13-Hydroxygermacrone 4,5-epoxide (**6**) was acetylated to give **7**, so the structure of **7** was determined to be 13-acetoxygermacrone 4,5-epoxide.

(4*S*,5*S*)-12-Acetoxygermacrone 4,5-epoxide (**8**), an oil, gave the molecular formula $C_{17}H_{24}O_4$. The ^{1}H- and ^{13}C-NMR spectra of **8** showed the presence of an acetoxymethyl group (δ 2.10 (s) and 63.9, 171.0, 20.7). The ^{1}H- and ^{13}C-NMR spectra of **8** showed similar signal patterns to those of **7**. But compound **8** gave a different peak from **7** on HPLC. This indicated that **8** is a geometrical isomer of **7** at the C-7,11 double bond. In a comparison of the ^{13}C-NMR spectra of **4**, **5**, **13**, **6**, **7**, **8** and **15** (shown in Table I), the vinyl methyl groups of **6** and **7**, assignable to 12-CH_3, appeared at 18.0 and 18.4 ppm, respectively. The other hand, a vinyl methyl of **8**, assignable to 13-Me, showed a different chemical shift (δ 16.3). It was considered that **6** and **7** were 13-hydroxy- and 13-acetoxygermacrone 4,5-epoxide, respectively, and **8** was 12-acetoxygermacrone 4,5-epoxide. The CD spectra of **6**, **7** and **8** gave a similar spectral pattern to that of **14** (shown in Fig. 2). This indicated that the absolute configurations and conformation of the ten-membered ring in **6**, **7** and **8** were the same as those of **14**.

Acetoxyneocurdione (**9**) gave the molecular formula $C_{17}H_{26}O_4$, from the MS. The IR spectrum of **9** showed the presence of an ester group (1740 cm^{-1}) and a ketone (1704 cm^{-1}). The ^{1}H-NMR spectrum of **9** showed the presence of two secondary methyl groups (δ 0.99 (3H, d, J=6.8 Hz), 1.06 (3H, d, J=7.0 Hz)), a vinyl methyl group (δ 1.67 (3H, s)), an olefinic proton (δ 5.12 (1H, t, J=7.0 Hz)) and an acetyl group (δ 2.06 (3H, s)). The ^{13}C-NMR spectrum of **9** showed the presence of an acetoxymethyl group (δ 170.6, 20.7, 67.4), and the carbon chemical shifts except for those of C-7, C-11, C-12 and C-13 were almost the same as those of neocurdione[1] (**15**) rather than those of curdione[10,11] (**16**) (Table I). The CD spectrum of **9** showed

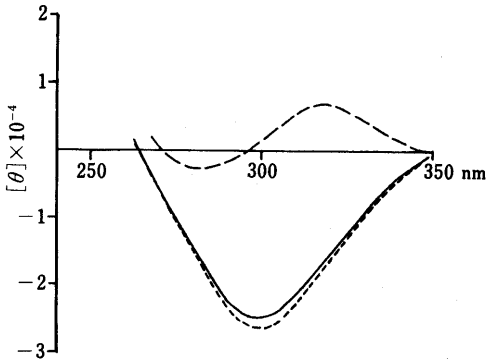

Fig. 3. CD Spectra of Curdione Derivatives
9, ——; **16**, – – –; **15**, ------.

a negative Cotton effect due to the β,γ-unsaturated ketone, which was superimposable on that of **15**, but was of opposite sign to that of **16** (Fig. 3). These facts indicated that **9** is the 12- or 13-acetoxy derivative of neocurdione and the configurations at C-4 and C-7 are 4*S* and 7*R*, respectively, the configuration at C-11 remains ambiguous.

Curcumadione (**10**) and isocurcumadione (**11**) gave the same molecular formula, $C_{15}H_{22}O_2$, from the MS (*m/z* 234 (M^+)). The ^{13}C-NMR spectrum of **10** and **11** showed the presence of two carbonyl groups (δ 208.1, 205.1 in **10** and 208.1, 191.0 in **11**), four olefinic carbons (δ 121.1, 134.7, 140.0, 143.7 in **10** and 126.7, 128.8, 144.8, 162.4 in **11**). The ^{1}H-NMR spectrum of **10** showed the presence of two olefinic methyl groups (δ 1.80 (s), 1.99 (s)), an acetyl group (δ 2.14 (s)), a secondary methl group (δ 1.07, J=6.8 Hz) and an olefinic proton (δ 5.52, t, J=6.6 Hz). These facts indicated that curcumadione is a seco-guaiane-type derivative (**10**) analogous to curcumenone.[12] The ^{1}H-NMR spectrum of **11** showed the presence of an acetyl group (δ 2.15 (s)), three vinyl methyl groups (δ 1.88, 1.92, 1.93) and one olefinic proton (δ 5.83 (q, J=1.3 Hz)) coupled with a vinyl methyl group. These data suggested that the structure of isocurcumadione is **11**. The absolute configurations of **10** and **11** have not been determined because the amounts of the samples were insufficient.

Experimental

All melting points were determined on a Yanagimoto melting point apparatus and are uncorrected. IR spectra were recorded on a JASCO A-202 grating infrared spectrometer. Optical rotations were recorded on a JASCO DIP-140 digital polarimeter. CD spectra were recorded on a JASCO J-20A spectropolarimeter. ^{1}H- and ^{13}C-NMR spectra were recorded on JEOL JNM FX-90Q and JEOL JNM GX-400 NMR spectrometers with tetramethylsilane as an internal standard (δ value, ppm). ^{1}H–^{1}H COSY and NOESY spectra were taken on a JEOL JNM GX-400 NMR spectrometer. MS were recorded on JEOL JMS D-100 and JEOL JMS 01SG-2 mass spectrometers. TLC was performed on precoated Silica gel 60F_{254} plates (Merck). Preparative layer chromatography (PLC) was performed on Silica gel PF_{254} (Merck, 200 × 200 × 0.7 mm). Column chromatography was performed on Silica gel type 60 (Merck). HPLC was performed on a reversed-phase column (YMC D-ODS-7) using various acetonitrile–H_2O solvent systems.

Isolation of the Sesquiterpenes As described in the previous paper,[1] ten sesquiterpenes were isolated from the chloroform-soluble fraction of the fresh rhizomes of *C. aromatica* (2 kg). The residual fraction after the previous isolation was subjected to repeated silica gel column chromatography using hexane–AcOEt gradient solvent systems, HPLC (YMC D-ODS-7) using an acetonitrile–H_2O system and PLC using hexane–AcOEt solvent systems to give epiprocurcumenol (**1**) (30 mg), isoprocurcumenol (**2**) (150 mg), neoprocurcumenol (**3**) (60 mg), (4*S*)-13-acetoxydehydrocurdione (**4**) (40 mg), (4*S*)-13-hydroxydehydrocurdione (**5**) (15 mg), (4*S*,5*S*)-13-hydroxygermacrone 4,5-epoxide (**6**) (30 mg), (4*S*,5*S*)-13-acetoxygermacrone 4,5-epoxide (**7**) (120 mg), (4*S*,5*S*)-12-acetoxygermacrone 4,5-epoxide (**8**) (25 mg), acetoxyneocurdione (**9**) (45 mg), curcumadione (**10**) (20 mg), isocurcumadione (**11**) (15 mg) and 13-hydroxygermacrone (**12**) (240 mg).

Epiprocurcumenol (1) Viscous oil. MS *m/z*: 234.163 (M^+) (Calcd for $C_{15}H_{22}O_2$: 234.162). $[\alpha]_D$ −20.5° (*c* = 0.3, MeOH). CD (*c* = 0.009, MeOH): $[\theta]_{355}$ +340, $[\theta]_{280}$ −13970, $[\theta]_{240}$ +4880. ^{1}H-NMR ($CDCl_3$): 1.37 (3H, s, 14-CH_3), 1.84 (3H, s, 13-CH_3), 1.94 (6H, s, 12-CH_3 and 15-CH_3)), 5.91 (1H, br s, 9-H). The ^{13}C-NMR data are given in Table I.

Isoprocurcumenol (2) Colorless needles, mp 99.5—100.5 °C (hexane). MS *m/z*: 234 (M^+) ($C_{15}H_{22}O_2$). *Anal.* Calcd for $C_{15}H_{22}H_2$: C; 76.88, H; 9.46. Found: C, 76.66; H, 9.50. IR ν_{max}^{KBr} cm^{-1}: 3450, 1674, 1610. $[\alpha]_D$ −62.5° (*c* = 0.2, MeOH). CD (*c* = 0.005, MeOH): $[\theta]_{321}$ −4043, $[\theta]_{248}$ +4942. ^{1}H-NMR ($CDCl_3$): 1.23 (3H, s, 14-CH_3), 1.82 (3H, s, 13-CH_3), 1.91 (3H, s, 12-CH_3), 4.90 (2H, br s, 15-H). The ^{13}C-NMR data are given in Table I.

Neoprocurcumenol (3) Colorless needles, mp 77—79 °C (hexane). MS *m/z*: 234 (M^+) ($C_{15}H_{22}O_2$). IR ν_{max}^{KBr} cm^{-1}: 3260, 1680, 1622, 1075. $[\alpha]_D$ +87.9° (*c* = 0.5, MeOH). CD (*c* = 0.02, MeOH): $[\theta]_{323}$ −2912, $[\theta]_{252}$ +13520. ^{1}H-NMR ($CDCl_3$): 1.12 (3H, s, 14-CH_3), 1.66, 1.81, 1.90 (3H each, s, CH_3-15, 12, 13). The ^{13}C-NMR data are given in Table I.

(4*S*)-13-Acetoxydehydrocurdione (4) Colorless needles, mp 77—78 °C (hexane). MS *m/z*: 292.166 (M^+) (Calcd for $C_{17}H_{24}O_4$, 292.166). IR ν_{max}^{KBr} cm^{-1}: 1740, 1715, 1695, 1230. $[\alpha]_D$ +313.5° (*c* = 0.3, MeOH). CD (*c* = 0.01, MeOH): $[\theta]_{317}$ +24718. ^{1}H-NMR ($CDCl_3$): 1.03 (3H, d, *J* = 6.9 Hz, 14-CH_3), 1.67 (3H, s, 14-CH_3), 1.77 (3H, s, 12-CH_3), 2.05 (3H, s, Ac), 3.04 (1H, d, *J* = 11.0 Hz, 6-H), 3.26 (1H, d, *J* = 11.0 Hz, 6-H), 3.23 (1H, d, *J* = 16.2 Hz, 10-H), 3.49 (1H, d, *J* = 16.2 Hz, 10-H), 4.47 (1H, d, *J* = 12.9 Hz, 13-H), 4.76 (1H, d, *J* = 12.9 Hz, 13-H), 5.11 (1H, dd, *J* = 6.0, 9.1 Hz, 1-H). The ^{13}C-NMR data are given in Table I.

(4*S*)-13-Hydroxydehydrocurdione (5) Colorless oil. MS *m/z*: 250 (M^+) ($C_{15}H_{22}O_3$). CD (*c* = 0.01, MeOH): $[\theta]_{307}$ +14305. ^{1}H-NMR ($CDCl_3$): 1.04 (3H, d, *J* = 6.6 Hz, 14-CH_3), 1.69 (3H, s, 12-CH_3), 1.84 (3H, s, 15-CH_3), 3.0—4.2 (m, 6-H, 9-H, 13-H), 5.12 (1H, t, *J* = 6.5 Hz, 1-H). The ^{13}C-NMR data are given in Table I.

(4*S*,5*S*)-13-Hydroxygermacrone 4,5-Epoxide (6) Viscous oil. MS *m/z*: 250.1564 (M^+) (Calcd for $C_{15}H_{22}O_3$: 250.1569). CD (*c* = 0.03, MeOH): $[\theta]_{311}$ +9735, $[\theta]_{249}$ +6560, $[\theta]_{229}$ −6325. ^{1}H-NMR ($CDCl_3$): 1.03 (3H, s, 14-CH_3), 1.72 (3H, s, 15-CH_3), 1.89 (3H, s, 12-CH_3), 4.23 (2H, s, 13-H), 5.22 (1H, br t, *J* = 6.8 Hz, 1-H). The ^{13}C-NMR data are given in Table I.

(4*S*,5*S*)-13-Acetoxygermacrone 4,5-Epoxide (7) MS *m/z*: 292.1676 (M^+) (Calcd for $C_{17}H_{24}O_4$: 292.1675). $[\alpha]_D$ +171.8° (*c* = 0.22, MeOH). ^{1}H-NMR ($CDCl_3$): 1.05 (3H, s, 14-CH_3), 1.73 (3H, s, 15-CH_3), 1.83 (3H, s, 12-CH_3), 2.10 (3H, s, Ac), 4.69 (2H, s, 13-H), 5.23 (1H, t, *J* = 7.5 Hz, 1-H). The ^{13}C-NMR data are given in Table I.

(4*S*,5*S*)-12-Acetoxygermacrone 4,5-Epoxide (8) Viscous oil. MS *m/z*: 292.1712 (M^+) (Calcd for $C_{17}H_{24}O_4$: 292.1675). $[\alpha]_D$ +118.4° (*c* = 0.05, MeOH). CD (*c* = 0.01, MeOH): $[\theta]_{306}$ +6837, $[\theta]_{249}$ +3874, $[\theta]_{224}$ −8660. ^{1}H-NMR ($CDCl_3$): 1.06 (3H, s, 14-CH_3), 1.73 (3H, s, 15-CH_3), 1.86 (3H, s, 13-CH_3), 2.10 (3H, s, Ac), 4.57 (2H, s, 12-H), 5.23 (1H, t, *J* = 7.5 Hz, 1-H). The ^{13}C-NMR data are given in Table I.

Acetoxyneocurdione (9) Colorless oil. MS *m/z*: 294.1869 (M^+) (Calcd for $C_{17}H_{26}O_4$: 294.1831). IR ν_{max}^{KBr} cm^{-1}: 1740, 1704, 1460, 1378. CD (*c* = 0.02, MeOH): $[\theta]_{298}$ −24806. ^{1}H-NMR ($CDCl_3$): 0.99 (3H, d, *J* = 6.8 Hz, 12- or 13-CH_3), 1.06 (3H, d, *J* = 7.0 Hz, 14-CH_3), 1.67 (3H, s, 15-CH_3), 2.06 (3H, s, Ac), 3.82 (2H, d, *J* = 5.7 Hz, 12- or 13-CH_2), 5.12 (1H, br t, *J* = 7.0 Hz, 1-H). The ^{13}C-NMR data are given in Table I.

Curcumadione (10) Colorless oil. MS *m/z*: 234.1625 (M^+) (Calcd for $C_{15}H_{22}O_2$: 234.1620). $[\alpha]_D$ +63.3° (*c* = 0.15, MeOH). ^{1}H-NMR ($CDCl_3$): 1.07 (3H, d, *J* = 6.8 Hz, 15-CH_3), 1.80, 1.99 (3H each, s, 12-, 13-CH_3), 2.14 (3H, s, 14-CH_3), 5.52 (1H, t, *J* = 6.6 Hz, 5-H). The ^{13}C-NMR data are given in Table I.

Isocurcumadione (11) Colorless oil. MS *m/z*: 234.1632 (M^+) (Calcd for $C_{15}H_{22}O_2$: 234.1620). ^{1}H-NMR ($CDCl_3$): 1.88, 1.92, 1.93 (3H each, s, 15, 12, 13-CH_3), 2.15 (3H, s, Ac), 2.43 (2H, t, *J* = 7.2 Hz, 3-H), 5.81 (1H, q, *J* = 1.3 Hz, 9-H). The ^{13}C-NMR data are given in Table I.

13-Hydroxygermacrone (12) Colorless needles, mp 59—61 °C (hexane). MS *m/z*: 234 (M^+) ($C_{15}H_{22}O_2$). ^{1}H-NMR ($CDCl_3$): 1.43, 1.66, 1.82 (3H each, s, 12, 14, 15-CH_3), 4.18 (1H, d, *J* = 12.2 Hz, 13-H), 4.67 (1H, d, *J* = 12.2 Hz, 13-H), 4.67 (1H, t, *J* = 7.6 Hz, 1-H), 4.99 (1H, br d, *J* = 10.7 Hz, 5-H). The ^{13}C-NMR data are given in Table I.

Acetylation of 13-Hydroxygermacrone 4,5-Epoxide (6) An excess of acetic anhydride was added to a solution of **6** (12 mg) in pyridine (0.5 ml) and the mixture was allowed to stand overnight at room temperature. The reaction solution was treated in the usual way and purified by silica gel column chromatography to give an acetate (**7**) (8 mg), which was identical with the natural **7** in terms of TLC and HPLC behavior, and ^{1}H- and ^{13}C-NMR spectra.

Acetylation of 13-Hydroxydehydrocurdione (5) **5** (5 mg) was acetylated and purified in the usual way to give an acetate (3 mg), which was identical with **5** in terms of TLC and HPLC behavior and ^{1}H-NMR spectrum.

***m*-Chloroperbenzoic Acid Oxidation of 12** A solution of **12** (4 mg) in $CHCl_3$ (2 ml) was treated with *m*-chloroperbenzoic acid (2.5 mg) at room termperature for 30 min. The reaction mixture was evaporated and the residue was purified by TLC to give racemic **6**, which was identical with the natural **6** in terms of TLC (solvent: hexane : ethyl acetate = 1 : 1) and HPLC (column; YMC D-ODS-7, 40% CH_3CN, t_R 5.4 min) behavior and the ^{1}H-NMR spectrum.

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